

The effects of vacuum-ultraviolet radiation on defects in low-k organosilicate glass  
(SiCOH) as measured with electron-spin resonance

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## ABSTRACT

Defect concentrations in SiCOH low-k dielectrics deposited on high-resistivity silicon substrates were measured with Electron Spin Resonance (ESR). CP4 and HF treatments were used in order to eliminate dangling bonds from the backside of the silicon substrate as well as the sample edges. Two kinds of defects with characteristic  $g = 2.0054 \sim 2.0050$  and  $g = 2.0018 \sim 2.0020$  were detected in pristine samples and quantified using Lorentzian fitting. The defect with the  $g$  factor of  $2.0054 \sim 2.0050$  is likely to be from the silicon-dangling bonds. The defect with the  $g$  factor of  $2.0018 \sim 2.0020$  is most likely from carbon-related centers. Upon exposure to VUV synchrotron radiation ( $h\nu = 12$  eV), the concentration of the silicon-dangling bonds is found to increase significantly.

## 1. Introduction

Silicon-based low-k dielectric materials have been widely used in microelectronic integrated circuits as interlayer dielectrics because that they can increase the speed by providing low capacitance to reduce interconnect delay (resistance-capacitance delay). However, in order to achieve a lower dielectric constant value, both carbon-doping and higher porosity are introduced, which often result in a variety of defects[1,2]. Therefore, it is important to measure and identify the defects as well as determine their concentrations.

Electron-spin resonance spectroscopy is a very effective tool to detect many defects in dielectrics and it has been applied to various high-k dielectrics, such as  $\text{HfO}_2$ . [3] However, ESR measurements have seldom been made on low-k organosilicate glass (SiCOH). One of the reasons is that ESR measurements usually require a high-resistivity substrate to maintain the high value of quality factor (Q factor) in the ESR cavity[4] or measurements in the liquid-He temperature range ( $\sim 4.3$  K) to freeze out dopants in silicon.[5,6] In this work, in order to obtain a clear spectroscopic signal, SiCOH was deposited on 250  $\mu\text{m}$  high-resistivity (3000  $\Omega\text{-cm}$ ) wafers. After this step, the ESR measurements were made with an X-band Bruker Eleksys 500E EPR spectrometer.

## 2. Theory

When a dielectric sample with certain defect states (unpaired electrons) is immersed in a radiofrequency modulated magnetic field, the defect states absorb energy through their magnetic susceptibility. The susceptibility of different defects is related to different relaxation mechanisms as a function of frequency. An electron-spin resonance experiment generally consists of measuring the absorption of microwave power at a fixed frequency as a function of an applied

laboratory magnetic field  $B$ . The physical factors which determine the ESR spectrum are most succinctly presented in terms of the so called spin Hamiltonian “ $H$ ”, it is possible to specialize to a spin Hamiltonian containing two terms:

$$H = \mu_B B \cdot g \cdot S + I \cdot A \cdot S(1)$$

where the first term is the electronic Zeeman interaction, and the second represents the hyperfine interaction between the electron of spin  $S$  and a single nucleus of spin  $I$ . In equation (1),  $\mu_B$  is the Bohr magneton  $\frac{e\hbar}{4\pi m_e}$  and  $A$  is the hyperfine tensor. The  $g$ -factor, which was measured in the experiments, has three principal-axis components. Relating the experimental spectra to equation (1) requires that the spin Hamiltonian be diagonalized to the so called “resonance condition”  $H_{res}$ .

For single-crystal samples, the ESR spectrum is usually obtained for rotations about one or more sample axes. These angular dependences are then fit to a resonance condition of the appropriate form, resulting in the values of the principal-axis components of  $g$ . However, in powdered or amorphous samples, all angular orientations are represented with equal probability. Averaging of the resonance condition over all angles results in a mathematically well-defined absorption envelope called the “powder pattern”. [7]

When dealing with amorphous samples, it is useful to define an effective  $g$  value corresponding to a particular value of  $H_{res}$  and the microwave frequency  $\nu$  according to the relation [8]:

$$g_{eff} \mu_B H_{res} = h\nu(2)$$

where  $h$  is Planck’s constant.

### 3. Experimental details

In this work, the thickness of the SiCOH films was 60 nm with a dielectric constant ( $k$ ) of 2.4. The sample was cut with a dicing saw into  $2.5 \times 20 \text{ mm}^2$  slices. SiCOH was deposited on 250  $\mu\text{m}$  high-resistivity (3000  $\Omega\text{-cm}$ ) wafers. In order to eliminate dangling bonds from the silicon substrate as well as edge defects, CP4 (HF: Nitric: Acetic)[9] and hydrofluoric acid (HF) treatments were used. The CP4 etch solution (50% HF: 70% Nitric: 100% Acetic) was primarily used to etch silicon and is commonly used to prepare electron spin resonance samples to remove surface and edge damage. The nitric acid oxidizes the silicon surface and the HF then removes the oxide. Acetic acid is used as a diluent, which improves the polishing effect of the etchant by preventing dissociation of  $\text{HNO}_3$ . A chemically stable wax (Crystalbond 590) was used to protect the SiCOH layer during CP4 etching, allowing the edges of the sample and the backside surface of the substrate to be placed into the CP4 solution without damaging the SiCOH.

To determine whether the defects measured by ESR are from SiCOH, the samples were treated in two ways before ESR measurement. The first method used HF before CP4 etching to etch the samples. The SiCOH was etched off by using a 5% (by volume) HF solution for 10 minutes. A reflectometer and a Fourier transform infrared spectrometer (FTIR) were used to determine when the SiCOH was fully removed. CP4 was then used to remove the defects from both the surfaces of the sample and the diced edges. The second method used CP4 alone. The chemically stable wax was used to glue two SiCOH layers face to face. The waxed assembly was then inserted into the etchant for 1 minute. The presence of the wax allowed etching only of the back surface of the substrate and the edges, thus leaving the SiCOH on the sample. A comparison can then be made between the samples prepared in these two ways to elucidate the defects in SiCOH.

#### 4. Results

ESR measurements showed that the samples with the SiCOH layer have a higher defect concentration than bare Si samples. In addition, samples with the same edge area but different surface areas could be made by adjusting the area of SiCOH that was covered by the wax. These partly covered samples have a smaller area of SiCOH but the same edge length. Following this, ESR measurements were made with the B field parallel to the sample normal. The results showed that the samples had lower defect concentrations compared with those samples that had larger SiCOH areas. The ESR spectra are shown in Figure 1. It can be easily seen that the amplitude of the “small area” signal is smaller than the “large area” signal. Since the edge lengths and substrate areas of these samples are the same, it is plausible that the defects measured by ESR are actually from SiCOH and/or its interface with the Si substrate, but not from the substrate backside or the edges.

The line shape of ESR spectra was found to be very nearly Lorentzian. Figure 2 shows a comparison of the observed line shape with Lorentzian and Gaussian fittings. The  $g$  value remained unchanged for both the Lorentzian and Gaussian fittings.

Experimentally, the first derivative of the absorption spectrum signal is written as a Lorentzian derivative. The integral of the Lorentzian distribution is used to determine the concentration of the defects. A 0.0003% KCl weak-pitch ( $10^{13}$  spins/cm) and DPPH (2,2-diphenyl-1-picrylhydrazyl) samples were used to calibrate the system.

To identify the defect states, the ESR signal was fitted with two defect states (Figure 3). The  $g$ -factors for these defect states were found to be 2.0054 and 2.0020 respectively. The defect with  $g = 2.0050 \sim 2.0054$  is likely to be either the silicon-dangling bonds in the bulk of the

SiCOH[10,11,12,13] or the Pb-type defects at the Si substrate/oxide interface under the SiOCH layer[6]. The g-value of the second defect ( $g = 2.0018 \sim 2.0020$ ) could be associated with the presence of either oxygen vacancies in the bulk of SiCOH[14] or carbon-related centers[15,16]. The defect concentration of the silicon dangling bonds was found to be about  $4.3 \times 10^{12}$  spins/cm<sup>2</sup> and the concentration of the carbon-related defects was  $1 \times 10^{12}$  spins/cm<sup>2</sup>.

In order to investigate the influence of vacuum ultraviolet (VUV) radiation on the defect concentration, samples were exposed to synchrotron radiation at the Taiwan National Radiation Research Center. The samples were exposed for either 10 or 40 minutes and the photon beam energy was 12 eV. The fluence was in the order of  $10^{15}$  photons/cm<sup>2</sup>. Following VUV exposure, ESR measurements were made. The ESR spectra (Figure 4) show that there were more silicon dangling bonds in the VUV-exposed samples than in the pristine samples. However, it is hard to identify the VUV influence on the carbon-related centers. This is because the defect concentrations of these centers are small compared with those of the silicon dangling bonds. Moreover, the ESR signal increased significantly with longer VUV exposure times. This observation importantly indicates that exposure of the low-k insulators to VUV radiation during lithographic patterning or plasma processing may impair their electrical properties by introducing additional defects.

The concentration of the silicon dangling bonds for 10 and 40 minutes exposure samples was 3.5 and 7.2 times higher compared with the concentrations in the pristine samples as shown in Table I.

TABLE 1. absolute values of the defect concentrations

	Defect state	concentration( $\text{cm}^{-2}$ )
pristine	silicon dangling bond	$4.3 \times 10^{12}$
12eV 10min exposed	silicon dangling bond	$1.5 \times 10^{13}$
12eV 40min exposed	silicon dangling bond	$3.1 \times 10^{13}$

## 5. Discussion and Conclusions

In summary, the defect concentrations in low-k SiCOH films deposited on high resistivity substrates could be detected by using electron spin resonance. Two types of defect states were detected by Lorentzian fitting: (1) silicon dangling bonds at  $g = 2.005$  and (2) defect centers at  $g = 2.002$  tentatively ascribed to carbon-related centers. In addition, VUV radiation increased the concentration of silicon dangling bonds in SiCOH. The defect concentration also increased with longer exposure time. This is likely caused by electron depletion by photoemission from defects during VUV irradiation.[17,18] That is, before VUV irradiation, the silicon dangling bonds are filled with electrons. The electrons are then depleted by photoemission during irradiation. Since the band gap for SiCOH is approximately 8 eV,[19] the 12 eV photons are able to generate electron photoemission. This VUV induced radiation damage was also observed in  $\text{SiO}_2/\text{Si}$  system: A VUV photon with energy larger than the band gap energy of  $\text{SiO}_2$  [8.9 eV, see T.H. DiStefano and D.E. Eastman, The band edge of amorphous  $\text{SiO}_2$  by photoinjection and photoconductivity measurements, Solid State Commun. **9**, (1971) 2259-2261] generates an electron-hole pair in the  $\text{SiO}_2$  film leading to positive oxide charging[add: R. J. Powell and G. F. Derbenwick, Vacuum ultraviolet radiation effects in  $\text{SiO}_2$ , IEEE Trans. Nucl. Sci. **NS-18**, (1971) 99-105, 20]. In addition, dangling bonds may be generated by photolysis of hydrogen from the

defect. This is consistent with the fact that the energy threshold for Si-H bond photolysis at the surface of H-passivated Si is  $\sim 7.9$  eV[21]. Moreover, VUV exposure can cause a loss of methylated species[22,23]. For example, 12eV VUV photons were able to cause Si-CH<sub>3</sub> depletion. It is possible that the loss of the -CH<sub>3</sub> group results in additional Si dangling bonds near the surface of the SiCOH films. Furthermore, VUV photons will produce holes in the SiOCH valence band which, upon trapping by defects, may generate ESR-active centers as it known to occur in SiO<sub>2</sub> layers thermally grown on silicon.[24]

Worth of adding here is that, contrary to the expectations, the revealed spectroscopic features of paramagnetic defects in the porous SiOCH-based low-k insulators differ from the defects routinely encountered in bulk amorphous SiO<sub>2</sub> [7,8,T. Endo, S. Taniguchi, I. Inaba, M. Katoh, M. Hayashi, K. Sugiyama, ESR centers in fused quartzexposed to glow discharge plasmas of Ar and H<sub>2</sub>, Jpn. J. Appl. Phys. **27**, (1988) 710-714; M. Kumeda, K. Nagano, T. Shimizu, Jpn. J. Appl. Phys. **29** (1990) 356-360; T.E. Tsai and D. E. Griscom, Experimental evidence for excitonic mechanism of defect generation in high-purity silica, Phys. Rev. Lett. **67** (1991) 2517-2520; H. Hosono, H. Kawazoe, N. Matsunami, Experimental evidence for Frenkel defect formation in amorphous SiO<sub>2</sub> by electronic excitation, Phys. Rev. Lett. **80** (1998) 317-320; H. Hosono, Y. Ikuta, T. Kinoshita, K. Kajihara, M. Hirano, Physical disorder and optical properties in the vacuum ultraviolet region of amorphous SiO<sub>2</sub>, Phys. Rev. Lett. **87** (2001) 175501] or in the SiO<sub>2</sub> layers thermally grown on Si [12, 24, H. S. Witham and P. M. Lenahan, The nature of deep hole trap in MOS oxides, IEEE Trans. Nucl. Sci. **34** (1987) 1147-1151] predominantly exhibiting E'-type signals with characteristic powder pattern and zero-crossing at  $g \approx 2.0005$  in the adsorption-derivative ESR spectra. This observation points towards different kind of precursor(s) activated during VUV exposure: If in bulk silica Si-Si bridges in the oxide



are hypothesized to be the most probable E'-center precursors [R. Thomon, H. Mizuno, Y. Ohki, K. Sasagane, K. Nagasawa, and Y. Hama, Correlation of the 5.0- and 7.6-eV absorption bands in SiO<sub>2</sub> with oxygen vacancy, Phys. Rev. B **39** (1989) 1337-1345] alternative bonding configurations involving Si and C atoms may be more relevant to the porous SiOCH layers. Upon VUV irradiation, the precursor activation may occur by dissociating the passivating hydrogen atom by hole trapping as it is found in the SiO<sub>2</sub> layers thermally grown on silicon [V. V. Afanas'ev and A. Stesmans, Charge state of paramagnetic E' center in thermal SiO<sub>2</sub> layers on silicon, J. of Physics: Condens. Matter **12** (2000) 2285-2290; V. Afanas'ev and A. Stesmans, Proton nature of radiation-induced positive charge in SiO<sub>2</sub> layers on Si, Europhys. Lett. **53** (2001)233-239]. Alternatively, bridging oxygen removal can also be relevant [ref to Hosono, - earlier mentioned PRLs] taking into account high VUV exposure ( $>10^{18}$ photons/cm<sup>2</sup>) and abundant hydrogen in the SiOCH film known to promote the damage [24].

## **6. Acknowledgments**

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## 7. Figure Captions

Figure 1. ESR spectra for pristine samples with same edge area but different SiCOH area. The defect concentration of the large-area sample is 1.24 times larger than that of the small-area sample.

Figure 2. Comparison of the observed ESR line shape with Lorentzian and Gaussian line shapes.

Figure 3. Measured ESR signals with defect-state fitting

Figure 4. ESR spectra for pristine and VUV-exposed samples

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